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EP-A- 0 021 003
EP-A- 0 023 758
EP-A- 0 129 106
EP-A- 0 147 074
EP-A- 0 178 495
US-A- 3 682 641
PATENT ABSTRACTS OF JAPAN, vol. 10, no.
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179 742 (FUJI SHASHIN FILM K.K.) 13-09-1985

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Description**Field of the Invention**

5 This invention relates to a novel method for developing positive photoresists, and more particularly to a process for developing alkali soluble resin/diazoketone photoresists so as to increase the developing rate difference, termed contrast, between the exposed and unexposed resist. The invention resides in the discovery that when a photoresist film is contacted with a aqueous solution of an organic base and a cationic surfactant prior to development in a aqueous solution of an organic base and a fluorochemical surfactant, the developing rate of the unexposed resist is virtually zero resulting in very high contrast. Furthermore the exposed photoresist develops cleanly to the substrate and the patterns have vertical edge profiles.

Description of the Prior Art

15 Photoresists are typically films which change their solubility response to a developer solution after exposure to an irradiation source, such as ultraviolet light. As a consequence of the exposure, a different dissolution rate in the developer exists between the exposed and unexposed (masked over) portions of the photoresist film thus producing the mask pattern in the photoresist film after development. Those photoresists which become more soluble in the exposed regions are referred to as positive photoresists and are the type addressed in this invention.

20 Positive photoresists typically consist of an aqueous alkaline soluble resin, such as novolac resin or poly-(p-hydroxystyrene), and a diazonaphthoquinone sulfonic acid ester dissolved in an organic solvent. The resist is usually applied by a spin casting technique to silicon wafers which may have a thin coating of silicon dioxide, aluminum, silicon nitride, glass or other material typically used in the fabrication of integrated circuits.

25 The coated wafers are exposed to light through a mask which provides a pattern for building the various circuit components on the wafer. The pattern is developed by dipping, spraying or placing a puddle of developer solution on the wafer.

The developer used is usually an aqueous base solution of either inorganic bases such as KOH, NaOH and Na_2SiO_3 or organic bases such as tetramethylammonium hydroxide and (2-hydroxyethyl)trimethylammonium hydroxide. The inorganic, metal ion containing bases are not preferred for integrated circuit patterning due to possible mobile ion contamination of the devices.

Typically, the alteration of the solubility of the photoresist in the developer is only a relative change; consequently, even the unexposed portions of the photoresist dissolve to some extent. Any process that enhances the developing rate difference between the relatively soluble exposed and relatively insoluble unexposed photoresist film is advantageous. It is highly desirable that during development there be as little attack as possible on the unexposed resist under conditions which lead to complete removal of exposed resist down to the substrate. The lower the dissolution rate of the unexposed resist relative to the exposed resist, the higher the contrast. High contrast gives a pattern with well defined vertical side walls and little change in the pattern over irregular surface topography.

40 Fluorocarbon and organic acid surfactants have been used with inorganic developers to achieve high contrast as disclosed in U. S. Patent Application Nos. 06/505,571 and 06/660,600, respectively. Likewise, quaternary ammonium surfactants have been used with organic base developers. However, in both cases the surfactant is quickly depleted, typically after just a single dip in the developer bath, thus losing high contrast imparted by the surfactant and making the process difficult to control. In addition, the organic base developer with the quaternary ammonium surfactant does not clean the residue from the exposed areas reliably.

Another developing method, disclosed in U. S. Patent No. 3,961,100, uses a double develop process without surfactants to improve the sensitivity and reduce the film loss resulting in higher contrast. This represents only a marginal improvement compared to the contrast achieved with this invention.

50 Another method, disclosed in U. S. Patent No. 4,212,935 employs an organic solvent soak to reduce the attack of the developer on the unexposed resist film. This treatment removes the lower molecular weight resin from the film and thus lowers the developing rate of the surface of resist. In the exposed areas the developing rate of the surface is still sufficient for the developer to break through to the underlying untreated resist. The result of such treatment is an undercut profile and little attack on the unexposed resist. The process is lengthy and difficult to control as disclosed in IBM Technical Bulletin, Vol. 27, No. 1A, pp. 377-378 (June, 1984). The solvents, particularly chlorobenzene, are hazardous to handle.

55 Other techniques have been disclosed for chemically treating the coated photoresist for generating the undercut profile for metal lift-off processes. Various such techniques are disclosed in U. S. Patent No. 4,212,935, but do not address the method and compositions disclosed in this invention in order to achieve high

contrast, no unexposed film loss and the other benefits of the process to be disclosed in this invention.

A need exists for an organic base, aqueous developer which is capable of providing a high contrast value (gamma) of at least five (5) without sacrificing sensitivity and which attains the foregoing advantages and minimizes the stated drawbacks.

5

CROSS-REFERENCE TO RELATED APPLICATIONS

References made to copending U. S. Patent Applications, Serial No. 767,318, filed on August 19, 1985, which is a Divisional Application of Serial No. 505,571, filed on June 17, 1983 (now abandoned) and which relates to a process of developing radiation sensitive positive resist films using a fluorocarbon surfactant containing developer solution and to U. S. Patent Application No. 660,600, filed on October 5, 1984, which relates to a process of developing radiation sensitive positive resist films using certain carboxylated surfactants.

10

SUMMARY OF THE INVENTION

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In accordance with the invention, it has been discovered that first contacting an exposed photoresist film with an aqueous solution consisting of an organic base and a cationic surfactant followed by a water rinse then contacting the photoresist film with an aqueous developer solution containing an organic base and a fluorocarbon surfactant gives very high contrast and clean patterns with vertical or, sometimes, undercut profiles.

20

This first or predip solution is neither sufficiently concentrated nor are the contact conditions sufficient to develop the photoresist. The developer solution, however, is sufficiently effective to develop the exposed photoresist in a time period of from a few seconds to a few minutes depending on the desired process.

25

The quaternary ammonium surfactant complexes with the resin to form a developer resistant layer. This barrier layer prevents the developer from attacking the unexposed resist while not sufficient to inhibit the attack of the developer on the exposed resist. Since the quaternary ammonium surfactant is in a predip bath, it is not depleted by complexing with the dissolved resin from the developing bath. The fluorocarbon surfactant in the developer bath aids the developing by making the developer more aggressive without increasing the base strength or concentration, thus the developer is able to clean out the patterns and eliminate the residue with no significant loss of sensitivity.

30

The photoresists employed with the developing process of the present invention are positive acting, i.e., those in which the exposed portions of the composition become more soluble upon exposure.

35

Suitable sensitizers used in positive photoresists of this kind are diazo ketones having diazo and keto groups at adjacent positions on the molecule, such as the quinone-diazide sulfonic acid derivatives. Suitable alkali soluble resins must be employed in the photoresists. Those contemplated by this invention are the prepolymerized phenolic-aldehyde resins, e.g., phenol formaldehyde, which are known as novolacs and are available commercially. Resins of this kind are disclosed, for example, in U.S. Patent 3,201,239; 3,868,254; 4,123,219 and 4,173,470, the disclosures of which are incorporated herein by reference. These phenolic-aldehyde resinous compounds must be soluble in organic solvents and aqueous alkaline solutions.

40

The predip bath consists of an aqueous solution of an organic base and a cationic surfactant. Bases that can be used belong to the general class of water soluble organic bases. Examples from the class are tetramethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide and tetra-(2-hydroxyethyl)ammonium hydroxide. This list is illustrative of the type of bases that can be used in the predip bath but should not be construed as being definitive.

45

The concentrations of base in the predip bath should be sufficiently low that there is no significant dissolution of the photoresist films resulting in measurable film loss in the exposed portion of the resist film. Since photoresists vary in the ease with which they dissolve in aqueous base solutions, it will be necessary to adjust the base concentration to the solubility characteristics of the resist. The concentration of base in the predip solution may range from 0.1% to 100% of the concentration of base in the developer. The preferred range is between 25 to 75% of the base strength in the developer. The most preferred range is about 50% of the base strength in the developer.

50

Following the predip treatment the photoresist film is rinsed then contacted with the developer. The base used in preparing the developer formulation may be selected from the general class of water soluble organic bases. Tetramethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide, tetra-(2-hydroxyethyl)ammonium hydroxide are illustrative of the types of bases that can be used in the developer but should not be considered definitive. Since photoresists vary in the ease with which they dissolve in aqueous base solutions, it will be necessary to adjust the base concentration to the solubility characteristics of the resist.

55

Following the process and using the compositions of the solutions of this invention imparts high contrast (gamma greater than 5) to positive photoresists of the diazonaphthoquinone photoactive compound/novolac

resin type photoresists with no unexposed photoresist film loss and no significant loss of sensitivity. The patterns produced by this process have vertical edge profiles and there is no residual resist on the substrate in the areas where the exposed resist was developed away.

5 DESCRIPTION OF THE PREFERRED EMBODIMENT

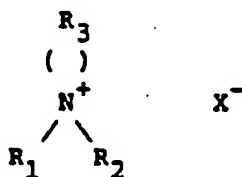
The invention constitutes a process of contacting a positive acting photoresist with a predip solution, rinsing the substrate, developing, rinsing and drying in order to obtain high contrast resulting in vertical profiles, high resolution capabilities, no unexposed resist film loss and good sensitivity. The compositions of the predip solution and developer solutions are critical to achieving the performance.

The process is used with a diazonaphthoquinone-type photoactive compound and novolac resin based photoresist. Typically, the photoresist is spin coated from solution on a silicon substrate or other such substrates used in the manufacture of integrated circuits or photomasks. The resist is then dried by baking at about 100°C for about 30 minutes in a convection oven; other baking processes, such as hot plate, will suffice. After the resist and substrate have cooled, the resist is irradiated by ultraviolet light or other actinic radiation to form a pattern of exposed and unexposed resist.

The resist coated substrate is then contacted with the predip solution for a time from 0.5 seconds to 30 minutes, more preferably from 10 seconds to 2 minutes, and most preferably one minute. The predip solution consists of, but is not limited to, an organic base and quaternary ammonium surfactant.

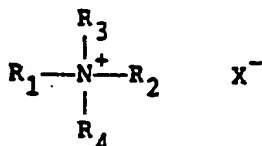
The base used in the predip solution may be selected from water soluble organic bases but more preferably from tetramethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide and tetra-(2-hydroxyethyl)ammonium hydroxide but most preferably tetramethylammonium hydroxide. The concentration of the base in the predip solution should be between 0.001 to 0.5N or more preferably from 0.05 to 0.3N.

The surfactants that can be used in the predip bath include compositions such as:



where R_3 is a cyclic group of from 2 to 6 carbons with from 0 to 3 heteroatoms chosen from the group O, N and S provided that each heteroatom is not bonded to another or a quaternary nitrogen. R_1 are saturated or unsaturated, straight or branched hydrocarbon chains of from 6 to 20 carbons. R_2 is the same as R_1 except has 1 to 120 carbon atoms. X^- may be Cl^- , I^- , Br^- , $CH_3SO_4^-$ or $CH_3CH_2SO_4^-$. An example of a member of this class is Example A in Table I.

Other surfactants that can be used in the predip bath include compositions such as:

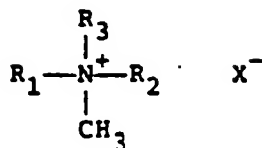


where R_1 and R_2 are as described above; R_3 is an alkyl group of between 1 and 4 carbons; and R_4 is a saturated or unsaturated straight or branched hydrocarbon chain of from 1 to 4 carbons, 1 to 4 quaternary ammonium groups of the formula:



wherein R_5 is a saturated or unsaturated straight or branched hydrocarbon chain of from 1 to 20 carbons, R_6 and R_7 are the same or different and each is an alkyl group of from 1 to 4 carbons, or phenalkyl wherein the alkyl moiety has from 0 to 3 carbons. Examples of members of this class are Example B and Example C in Table I.

Other surfactants that can be used in the predip bath include compositions such as:



where R_3 is a hydrocarbon chain derived from coconut oils. R_1 and R_2 are hydroxy alkyl groups containing between 1 and 4 carbons. An example of this class of compound is Example D in Table I.

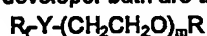
The concentration of cationic surfactant in the predip bath may be from 0.0001 to 1.0% by weight of the predip bath. The preferred concentration range is between 0.001 and 0.75% and the most preferred range is between 0.01 and 0.25%.

The substrate is then rinsed for a minimum period of time preferably greater than 10 seconds with deionized water and more preferably for one minute.

The substrate is then contacted with the developer solution until the resist that received proper exposure has dissolved cleanly away with no unexposed resist loss and more preferably for at least 10 seconds and most preferably more than 60 seconds.

The developer solution consists of, but is not limited to, an organic base and fluorocarbon surfactant. The base used in the developer solution may be selected from water soluble organic bases, and more preferably tetramethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide and tetra-(2-hydroxyethyl)ammonium hydroxide, but most preferably tetramethylammonium hydroxide. Preferably, the base in the developer and in the predip are the same.

The surfactants that can be used in the developer bath are those characterized by formula:



where Y is a radical selected from the group $-CH_2CH_2O-$, $-SO_2NR'-$, $-SO_3-$, $-SO_2N(R')CH_2CO_2-$, $-CO_2-$ and $-CO-NR'-$ wherein R_f is either a straight or branched chain of the formula C_pF_{2p+1} where p is an integer from 3 to 17; and wherein R is hydrogen or an acyl or alkyl radical of 1 to 30 carbon atoms and m is an integer of 2 to 26 and preferably where m is an integer of 5 to 26, and R' is hydrogen or an alkyl radical of 1 to 6 carbon atoms. The surfactant in the developer may be selected from those mentioned above but more preferably from those in Table II and most preferably Example A from Table II.

The developer bath operates at a pH of at least 9 and preferably at a pH above about 10.5 and most preferably above a pH of 12. The concentration of the organic base in the developer must be varied depending on the solubility characteristics of the photoresist and on the developing process in order to obtain the desired sensitivity without unexposed photoresist film loss. The concentrations of the base in the developer solution should be between 0.05 to 1N or more preferably from 0.1 to 0.5N.

The concentration of fluorocarbon surfactant in the developer may be in the range from 0.001 to 5% by weight of the total developer solution. The preferred range is 0.005 to 2%.

The following examples are illustrative of the invention. The enumeration of details in the examples should not be interpreted as a limitation on the invention except as may be expressed in the appended claims.

PREPARATION OF THE PHOTORESIST FOR DEVELOPING

The wafers were coated, prebaked and exposed in a conventional manner. The following is provided as typical.

The photoresist coating was prepared by spin coating the resist solution on a silicon wafer substrate. The silicon wafer had been subjected to a 200°C dehydration bake for sixteen (16) hours; and then treated with a 50% hexamethyldisilazane solution in xylene for twenty seconds immediately prior to applying the photoresist for coating. The wafers were spun so as to provide a 1 micrometer (μm) thick film. The coated wafers were baked at 100°C for 30 minutes in a forced air convection oven. After baking, the wafers were exposed to ultraviolet light through step tablet resolution mask with windows of various optical density so as to provide various exposure levels on the same wafer. The incident exposure was a range of exposure from no exposure to sufficient exposure for the resist to develop to the substrate. The contrast was determined from the slope of a line drawn parallel to the descending portion of a plot of the normalized film thickness remaining after developing vs. the common logarithm of the exposure.

DEVELOPING THE PHOTORESIST

The resist films in the following examples were prepared for developing as described above.

EXAMPLE 1

(Comparativ)

5 The photoresist was contacted with a 0.378N tetramethylammonium hydroxide aqueous base solution containing 1% by weight of the total solution of the surfactant in Example A of Table II for 75 seconds at 25°C. The substrate was then rinsed in deionized water for 60 seconds and dried with nitrogen. The results are shown in Table III.

EXAMPLE 2

(Comparative)

15 The photoresist was contacted with deionized water for 60 seconds at 22°C and then developed as described in Example 1. The results are shown in Table III.

EXAMPLE 3

(Comparative)

20 The photoresist was contacted with a 0.189N tetramethylammonium hydroxide aqueous base solution for 30 seconds at 25°C. The substrate was rinsed with deionized water for 60 seconds, then developed in the developer as described in Example 1. The results are shown in Table III.

EXAMPLE 4

25 The photoresist was contacted with a 0.189N tetramethylammonium hydroxide aqueous base solution containing 0.0025% by weight of the total solution of the surfactant in Example A of Table I for 30 seconds at 25°C. The substrate was rinsed with deionized water for 60 seconds, then developed in the developer as described in Example 1. The results are shown in Table III.

EXAMPLE 5

35 The photoresist was contacted with a 0.189N tetramethylammonium hydroxide aqueous base solution containing 0.0015% by weight of the total solution of the surfactant in Example B of Table I for 30 seconds at 25°C. The substrate was rinsed with deionized water for 60 seconds, then developed in the developer as described in Example 1. The results are shown in Table III.

EXAMPLE 6

40 The photoresist was contacted with a 0.189N tetramethylammonium hydroxide aqueous base solution containing 0.002% by weight of the total solution of the surfactant in Example C of Table I for 30 seconds at 25°C. The substrate was rinsed with deionized water for 60 seconds, then developed in the developer as described in Example 1. The results are shown in Table III.

EXAMPLE 7

45 The photoresist was contacted with a 0.189N tetramethylammonium hydroxide aqueous base solution containing 0.005% by weight of the total solution of the surfactant in Example D of Table I for 30 seconds at 25°C. The substrate was rinsed with deionized water for 60 seconds, then developed in the developer as described in Example 1. The results are shown in Table III.

TABLE I

SURFACTANT

EXAMPLE SURFACTANT

A

$$\begin{array}{c} \text{C}_6\text{H}_{13} \quad \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \text{N}^+ \\ \quad \quad \diagdown \quad \diagup \\ \text{C}_2\text{H}_5 \quad \text{CH}_2 - \text{CH}_2 \end{array} \quad \text{O}$$

$$\text{C}_2\text{H}_5 - \text{SO}_4^-$$

B

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}_{16}\text{H}_{31} - \text{N}^+ - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

$$\text{Cl}^-$$

C

$$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ | \quad \quad | \\ \text{C}_{14}\text{H}_{29} - \text{N}^+ - (\text{CH}_2) - \text{N}^+ - \text{CH}_3 \\ | \quad \quad | \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array} \quad \text{Cl}^- \quad \text{Cl}^-$$

D

$$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ | \\ \text{C}_8\text{H}_{18} - \text{N}^+ - \text{CH}_2\text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array} \quad \text{Cl}^-$$

Example	fluorosurfactant	<u>TABLE II</u>
1	1	1
2	2	2
3	3	3
4	4	4
5	5	5
6	6	6
7	7	7
8	8	8
9	9	9
10	10	10
11	11	11
12	12	12
13	13	13
14	14	14
15	15	15
16	16	16
17	17	17
18	18	18
19	19	19
20	20	20
21	21	21
22	22	22
23	23	23
24	24	24
25	25	25
26	26	26
27	27	27
28	28	28
29	29	29
30	30	30
31	31	31
32	32	32
33	33	33
34	34	34
35	35	35
36	36	36
37	37	37
38	38	38
39	39	39
40	40	40
41	41	41
42	42	42
43	43	43
44	44	44
45	45	45
46	46	46
47	47	47
48	48	48
49	49	49
50	50	50
51	51	51
52	52	52
53	53	53
54	54	54
55	55	55
56	56	56
57	57	57
58	58	58
59	59	59
60	60	60
61	61	61
62	62	62
63	63	63
64	64	64
65	65	65
66	66	66
67	67	67
68	68	68
69	69	69
70	70	70
71	71	71
72	72	72
73	73	73
74	74	74
75	75	75
76	76	76
77	77	77
78	78	78
79	79	79
80	80	80
81	81	81
82	82	82
83	83	83
84	84	84
85	85	85
86	86	86
87	87	87
88	88	88
89	89	89
90	90	90
91	91	91
92	92	92
93	93	93
94	94	94
95	95	95
96	96	96
97	97	97
98	98	98
99	99	99
100	100	100

40

A $\text{CF}_3(\text{CF}_2)_6-\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_4\text{H}$

B $\text{CF}_3(\text{CF}_2)_5-\text{CO}-\text{N}(\text{CH}_3)-(\text{CH}_2\text{CH}_2\text{O})_{12}-\text{CH}_3$

C $\text{CF}_3(\text{CF}_2)_3-\text{SO}_2-\text{NH}-(\text{CH}_2\text{CH}_2\text{O})_{14}-\text{CH}_3$

45

D $\text{CF}_3(\text{CF}_2)_8-\text{SO}_2-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_8-\text{CH}_3$

E $\text{CF}_3(\text{CF}_2)_5-\text{CO}_2-(\text{CH}_2\text{CH}_2\text{O})_9-\text{C}_4\text{H}_9$

50

F $\text{CF}_3(\text{CF}_2)_7-\text{SO}_2-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2\text{CH}_2\text{O})_{15}-\text{CO}-\text{C}_{14}\text{H}_{29}$

55

G $\text{CF}_3(\text{CF}_2)_8-\text{SO}_2-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CO}_2-(\text{CH}_2\text{CH}_2\text{O})_{10}-\text{C}_{11}\text{H}_{23}$

TABLE III

EXAMPLE	SENSITIVITY (mJ/cm ²)	CONTRAST (gamma)	FILM LOSS (%)	WALL ANGLE (°)
1	30	1.6	6	80
2	30	1.6	6	80
3	25	1.8	7	80
4	35	5.2	0	90
5	37	6	0	90
6	42	5	0	90
7	45	4.8	0	90

The invention has been particularly described with reference to preferred embodiments thereof; it will be understood by those skilled in the art, however, that changes in form and details may be made therein without departing from the spirit and scope of the invention.

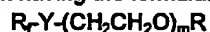
Claims

1. A process for developing a positive radiation sensitive resist film comprised of quinone diazide sulfonic acid derivatives and alkali soluble resin that has been coated on a substrate and exposed to radiation to form a surface relief pattern which comprises:

(a) contacting the exposed film with a solution comprising an organic base aqueous solution adjusted to a concentration that does not give development of the photoresist and containing a cationic surfactant from about 0.0001 to about 1.0% and more preferably from about 0.001 to about 0.75% and most preferably 0.01 to 0.25% by weight of the total solution.

(b) subjecting said film to an aqueous rinse, and

(c) contacting the said film with an organic aqueous base developer solution having a pH of at least 9 and containing from about 0.0001 to 5% and more preferably from about 0.001 to about 2% based on the weight of developer of a fluorocarbon surfactant having the formula:

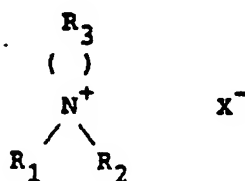


where Y is a radical selected from the group $-CH_2CH_2O-$, $-SO_2NR'-$, $-SO_3-$, $-SO_2N(R')CH_2CO_2-$, $-CO_2-$ and $-CO-NR'-$ wherein R_f is either a straight or branched chain of the formula C_pF_{2p+1} where p is an integer of from 3-17 and wherein R is hydrogen or an acyl or alkyl radical of 1 to 30 carbon atoms and m is an integer of 2 to 26 and preferably where m is an integer of 5-26, and R' is hydrogen or an alkyl radical of 1-6 carbon atoms until the exposed portions of the film are dissolved.

2. The process in Claim 1 in which the organic base in Step (a) is tetramethylammonium hydroxide.

3. The process in Claim 1 in which the organic base in Step (a) is (2-hydroxyethyl)trimethylammonium hydroxide.

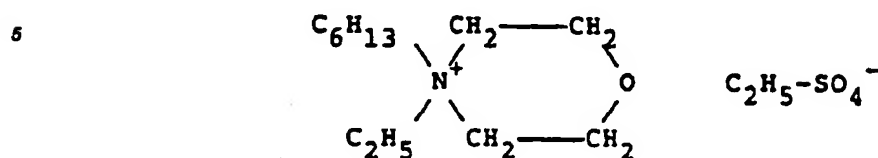
4. The process of Claim 1 in which the cationic surfactant in Step (a) comprises a compound selected from those having the formula:



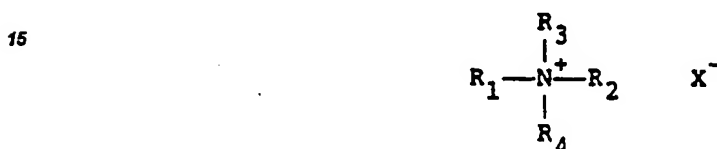
where R_3 is a cyclic group of from 2 to 6 carbons with from 0 to 3 heteroatoms chosen from the group O, N and S provided that each heteroatom is not bonded to another or a quaternary nitrogen. R_1 are saturated or unsaturated, straight or branched hydrocarbon chains of from 6 to 20 carbons. R_2 is the same as R_1 except has 1 to

120 carbon atoms. X^- may be Cl^- , I^- , Br^- , $CH_3SO_4^-$ or $CH_3CH_2SO_4^-$.

5. The process of Claim 4 in which the cationic surfactant in Step (a) comprises:

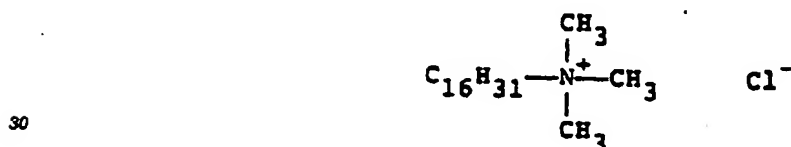


6. The process of Claim 1 in which the cationic surfactant in Step (a) comprises a compound selected from those having the formula:



where R_1 and R_2 are as described above; R_3 is an alkyl group of between 1 and 4 carbons; and R_4 is a saturated or unsaturated straight or branched hydrocarbon chain of from 1 to 4 carbons or phenalkyl wherein the alkyl moiety has from 0 to 3 carbons.

7. The process of Claim 6 in which the cationic surfactant in Step (a) comprises:

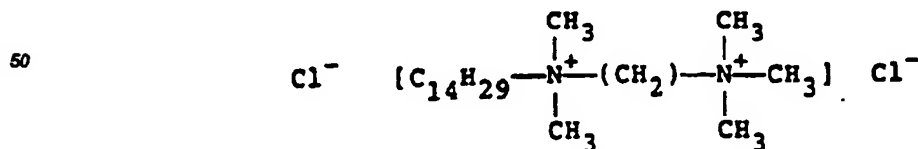


8. The process of Claim 1 in which the cationic surfactant in Step (a) comprises a compound selected from those having the formula:

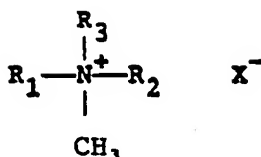


where R_1 , R_2 , and R_3 are as described above. R_4 is a saturated or unsaturated straight or branched hydrocarbon chain containing 1 to 4 quaternary ammonium groups $-(N^+R_5R_6R_7)$ wherein R_5 is a saturated or unsaturated straight or branched hydrocarbon chain of from 1 to 20 carbons, R_6 and R_7 are the same or different and each is an alkyl group of from 1 to 4 carbons.

9. The process of Claim 8 in which the cationic surfactant in Step (a) comprises:

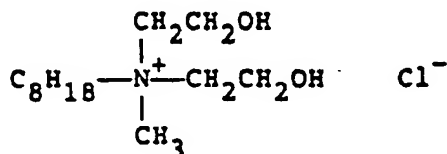


10. The process of Claim 1 in which the cationic surfactant in Step (a) comprises a compound selected from those having the formula:



where R_3 is a hydrocarbon chain derived from coconut oils. R_1 and R_2 are hydroxy alkyl groups containing between and 4 carbons.

11. The process of Claim 10 in which the cationic surfactant in Step (a) comprises:



12. The process in Claim 1 in which the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

13. The process in Claim 1 in which the organic base in Step (c) is tetramethylammonium hydroxide.

14. The process in Claim 1 in which the organic base in Step (c) is (2-hydroxyethyl)trimethylammonium hydroxide.

15. The process in Claim 4 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

16. The process in Claim 5 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

17. The process in Claim 6 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

18. The process in Claim 7 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

19. The process in Claim 8 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

20. The process in Claim 9 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

21. The process in Claim 10 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

22. The process in Claim 11 in which the organic base in Steps (a) and (c) is tetramethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

23. The process in Claim 4 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

24. The process in Claim 5 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

25. The process in Claim 6 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

26. The process in Claim 7 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

27. The process in Claim 8 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

28. The process in Claim 9 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

29. The process in Claim 10 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

30. The process in Claim 11 in which the organic base in Steps (a) and (c) is (2-hydroxyethyl)trimethylammonium hydroxide and the surfactant in Step (c) is $CF_3(CF_2)_6-CH_2CH_2O-(CH_2CH_2O)_4H$.

Patentanspruch

1. Verfahren zur Entwicklung eines strahlungssensitiven Positivlackfilms, der Chinondiazidsulfonsäurederivate und alkalilösliches Harz enthält, und der auf ein Substrat aufgebracht und mit Strahlung belichtet wurde, um ein räumliches Oberflächenmuster herzustellen, umfassend:

(a) Kontaktieren des belichteten Films mit einer Lösung, die eine wässrige Lösung einer organischen Base enthält und auf eine Konzentration eingestellt ist, die nicht zur Entwicklung des Photolacks führt, und ein kationisches oberflächenaktives Mittel von etwa 0,0001 bis etwa 1,0%, vorzugsweise von etwa 0,001 bis etwa 0,75% und besonders bevorzugt 0,01 bis 0,25 Gew.-% der gesamten Lösung enthält,

10 (b) wäßriges Spülen des Films und

(c) Kontaktieren des Films mit einer organischen wäßrigen Basenentwickler-Lösung, die einen pH von mindestens 9 aufweist und von etwa 0,0001 bis 5% und vorzugsweise von etwa 0,001 bis etwa 2% auf Basis des Entwickler-Gewichts an einem oberflächenaktiven Fluorkohlenwasserstoff enthält, mit der Formel:



15 bei der Y ein Rest ist, ausgewählt aus der Gruppe $-\text{CH}_2\text{CH}_2\text{O}-$, $-\text{SO}_2\text{NR}'$, $-\text{SO}_3-$, $-\text{SO}_2\text{N}(\text{R}')\text{CH}_2\text{CO}_2-$, $-\text{CO}_2-$ und $-\text{CO}-\text{NR}'$, worin R_2 entweder eine gerade oder eine verzweigte Kette der Formel $\text{C}_p\text{F}_{2p+1}$ ist, bei der p eine ganze Zahl von 3-17 ist und worin R Wasserstoff oder ein Acyl- oder Alkylrest mit 1 bis 30 Kohlenstoffatomen ist, und m eine ganze Zahl von 2 bis 26 ist, und wo vorzugsweise m eine ganze Zahl von 5-26 ist, und R' Wasserstoff oder ein Alkylrest mit 1-6 Kohlenstoffatomen ist, bis die belichteten Teile des
20 Films aufelöst sind.

2. Verfahren nach Anspruch 1, worin die organische Base in Schritt (a) Tetramethylammoniumhydroxid ist.

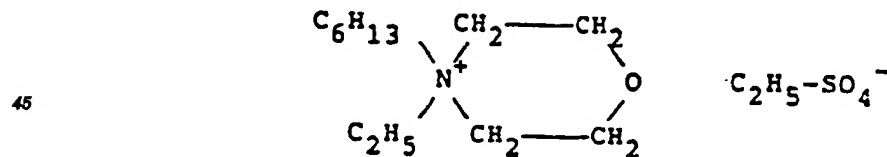
2. Verfahren nach Anspruch 1, worin die organische Base in Schritt (a) (2-Hydroxyethyl)trimethylammoniumhydroxid ist.

4. Verfahren nach Anspruch 1, worin das kationische oberflächenaktive Mittel in Schritt (a) eine Verbindung enthält, ausgewählt aus solchen mit der Formel:

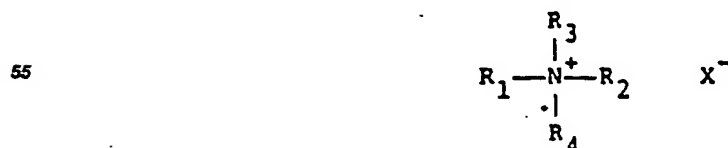


35 worin R_3 eine zyklische Gruppe von 2 bis 6 Kohlenstoffatomen mit von 0 bis 3 Heteroatomen, ausgewählt aus der Gruppe O, N und S ist, vorausgesetzt, daß jedes Heteroatom nicht an ein anderes oder an einen quaternären Stickstoff gebunden ist, R_1 gesättigte oder ungesättigte, gerade oder verzweigte Kohlenwasserstoffketten von 6 bis 20 Kohlenstoffatomen sind, R_2 gleich wie R_1 ist, außer daß er 1 bis 120 Kohlenstoffatome hat, und wobei X^- Cl^- , F^- , Br^- , $CH_3SO_4^-$ oder $CH_3CH_2SO_4^-$ sein kann.

40 5. Verfahren nach Anspruch 4, worin das kationische oberflächenaktive Mittel in Schritt (a):

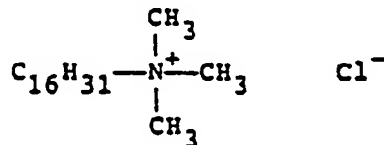
**enthält**

50 **6. Verfahren nach Anspruch 1, worin das kationische oberflächenaktive Mittel in Schritt (a) eine Verbindung enthält, ausgewählt aus solchen mit der Formel:**



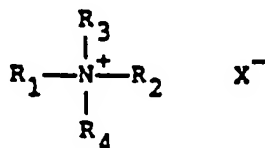
worin R_1 und R_2 wie oben beschrieben sind, R_3 eine Alkylgruppe zwischen 1 und 4 Kohlenstoffatomen ist und R_4 eine gesättigte oder ungesättigte, gerade oder verzweigte Kohlenwasserstoffkette von 1 bis 4 Kohlenstoffatomen oder Phenylalkyl ist, worin die Alkylgruppe von 0 bis 3 Kohlenstoffatomen hat.

7. Verfahren nach Anspruch 6, worin das kationische oberflächenaktive Mittel in Schritt (a):



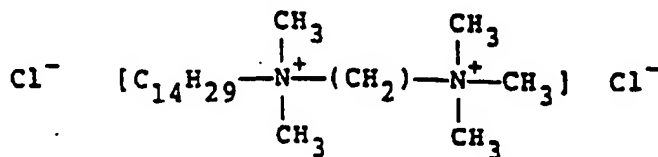
enthält.

8. Verfahren nach Anspruch 1, worin das kationische oberflächenaktive Mittel in Schritt (a) eine Verbindung enthält, ausgewählt aus solchen mit der Formel:



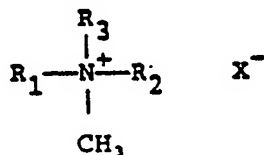
worin R_1 , R_2 und R_3 wie oben beschrieben sind, R_4 eine gesättigte oder ungesättigte, gerade oder verzweigte Kohlenwasserstoffkette ist, die 1 bis 4 quaternäre Ammoniumgruppen $-(\text{N}^+\text{R}_5\text{R}_6\text{R}_7)$ enthält, worin R_5 eine gesättigte oder ungesättigte, gerade oder verzweigte Kohlenwasserstoffkette von 1 bis 20 Kohlenstoffatomen ist, R_6 und R_7 gleich oder verschieden sind, und jeder eine Alkylgruppe von 1 bis 4 Kohlenstoffatomen ist.

9. Verfahren nach Anspruch 8, worin das kationische oberflächenaktive Mittel in Schritt (a):



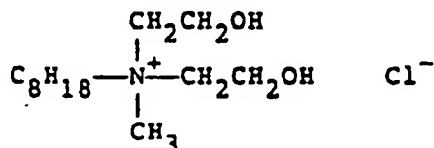
enthält.

10. Verfahren nach Anspruch 1, worin das kationische oberflächenaktive Mittel in Schritt (a) eine Verbindung enthält, ausgewählt aus solchen mit der Formel:



worin R_3 eine aus Kokosnußölen stammende Kohlenwasserstoffkette ist, und R_1 und R_2 Hydroxyalkylgruppen sind, die zwischen 1 und 4 Kohlenstoffatome enthalten.

11. Verfahren nach Anspruch 10, worin das kationische oberflächenaktive Mittel in Schritt (a):



enthält.

12. Verfahren nach Anspruch 1, worin das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

13. Verfahren nach Anspruch 1, worin die organische Base in Schritt (c) Tetramethylammoniumhydroxid ist.

14. Verfahren nach Anspruch 1, worin die organische Base in Schritt (c) (2-Hydroxyethyl)trimethylammoniumhydroxid ist.

15. Verfahren nach Anspruch 4, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

16. Verfahren nach Anspruch 5, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

17. Verfahren nach Anspruch 6, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

18. Verfahren nach Anspruch 7, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

19. Verfahren nach Anspruch 8, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

20. Verfahren nach Anspruch 9, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

21. Verfahren nach Anspruch 10, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

22. Verfahren nach Anspruch 11, worin die organische Base in den Schritten (a) und (c) Tetramethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

23. Verfahren nach Anspruch 4, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

24. Verfahren nach Anspruch 5, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

25. Verfahren nach Anspruch 6, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

26. Verfahren nach Anspruch 7, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

27. Verfahren nach Anspruch 8, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

28. Verfahren nach Anspruch 9, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

29. Verfahren nach Anspruch 10, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

30. Verfahren nach Anspruch 11, worin die organische Base in den Schritten (a) und (c) (2-Hydroxyethyl)trimethylammoniumhydroxid und das oberflächenaktive Mittel in Schritt (c) $\text{CF}_3(\text{CF}_2)_6\text{-CH}_2\text{CH}_2\text{O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ ist.

Revendications

1. Procédé pour le développement d'une photoréserve positive sensible à l'irradiation constituée par des dérivés de l'acide sulfonique quinone-diazide et de résine alcalino-soluble qui ont été revêtus d'un substrat et exposés à l'irradiation pour former un dessin en relief qui comprend les étapes consistant à :

a) mettre en contact le film exposé avec une solution comprenant une solution aqueuse de base organique ajustée à une concentration qui ne donne pas le développement de la photoréserve et contenant un agent tensioactif cationique d'environ 0,0001 jusqu'à environ 1,0 % et de façon plus préférée d'environ 0,001 jusqu'à environ 0,75 % et de façon plus préférée de 0,01 jusqu'à 0,25 % en poids de la solution totale.

b) soumettre le film à un rinçage aqueux, et

c) mettre en contact le film avec une solution de révélateur de base aqueuse organique ayant un pH d'au moins 9 et contenant environ 0,0001 jusqu'à 5 % et de façon plus préférée d'environ 0,001 jusqu'à environ 2 % en poids rapporté au poids du révélateur d'un agent tensioactif fluorocarboné ayant la formule :

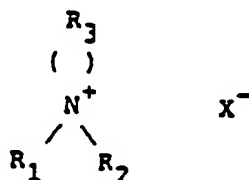
$$R_f-Y-(CH_2CH_2O)_mR$$

dans laquelle Y est un radical choisi parmi le groupe $-\text{CH}_2\text{CH}_2\text{O}-$, $-\text{SO}_2\text{NR}'-$, $-\text{SO}_3-$, $-\text{SO}_2\text{N}(\text{R}')\text{CH}_2\text{CO}_2-$, $-\text{CO}_2-$ et $-\text{CO}-\text{NR}'-$ où R_1 est soit une chaîne rectiligne ou ramifiée de formule $\text{C}_p\text{F}_{2p+1}$ dans laquelle p est un nombre entier de 3-17 et dans laquelle R est l'hydrogène ou un radical acyle ou alkyle de 1 à 30 atomes de carbone et m est un nombre entier de 2 jusqu'à 26 et de préférence où m est un nombre entier de 5-26 et R' est l'hydrogène ou un radical alkyle de 1-6 atomes de carbone jusqu'à dissolution des portions exposées du film.

2. Procédé selon la revendication 1, dans lequel la base organique de l'étape (a) est de l'hydroxyde de tétraméthylammonium.

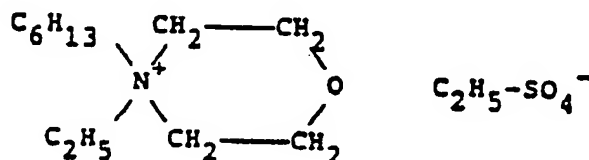
3. Procédé selon la revendication 1, dans lequel la base organique dans l'étape (a) est l'hydroxyde de (2-hydroxyéthyl)triméthylammonium.

4. Procédé selon la revendication 1, dans lequel l'agent tensioactif cationique de l'étape (a) comprend un composé choisi parmi ceux avant la formule :

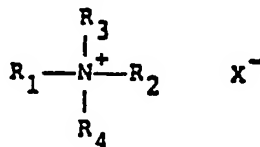


dans laquelle R_3 est un groupe cyclique de 2 à 6 atomes de carbone avec de 0 à 3 hétéroatomes choisis parmi le groupe O, N et S dans la mesure où chaque hétéroatome n'est pas lié à un autre ou à un azote quaternaire. R_1 représente des chaînes saturées ou non saturées, rectilignes ou ramifiées hydrocarbonées de 6 à 20 atomes de carbone. R_2 est identique à R_1 sauf qu'il possède 1 à 120 atomes de carbone. X⁻ peut être Cl⁻, I⁻, Br⁻, $CH_3SO_4^-$ ou $CH_3CH_2SO_4^-$.

5. Procédé selon la revendication 4, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par :

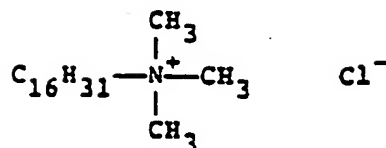


6. Procédé selon la revendication 1, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par un composé choisi parmi ceux ayant la formule :



dans laquelle R₁ et R₂ sont tels que décrit ci-dessus ; R₃ est un groupe alkyle comprenant entre 1 et 4 atomes de carbone ; et R₄ est une chaîne hydrocarbonée saturée ou non saturée, rectiligne ou ramifiée de 1 à 4 atomes de carbone ou phénylalkyl où la parti alkyle possède de 0 à 3 atomes d carbone.

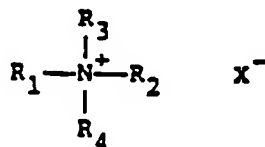
7. Procédé selon la revendication 6, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par :



5

8. Procédé selon la revendication 1, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par un composé choisi parmi ceux ayant la formule :

10



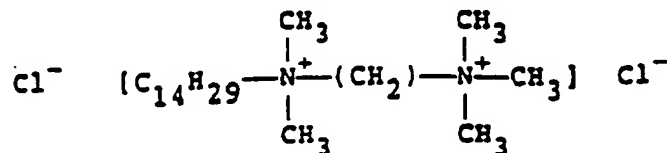
15

où R_1 , R_2 et R_3 sont tels que décrits ci-dessus. R_4 est une chaîne hydrocarbonée saturée ou insaturée, rectiligne ou ramifiée contenant 1 à 4 groupes d'ammonium quaternaire ($\text{N}^+\text{R}_5\text{R}_6\text{R}_7$) où R_5 est une chaîne hydrocarbonée saturée ou insaturée rectiligne ou ramifiée de 1 à 20 atomes de carbone, R_6 et R_7 sont identiques ou différents et chacun est un groupe alkyle de 1 à 4 atomes de carbone.

20

9. Procédé selon la revendication 8, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par :

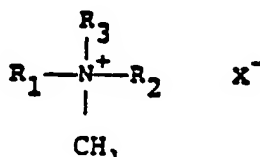
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10. Procédé selon la revendication 1, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par un composé choisi parmi ceux ayant la formule :

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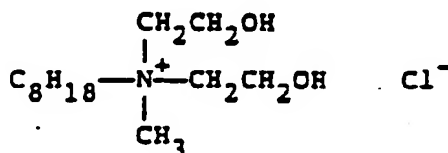


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où R_3 est une chaîne hydrocarbonée dérivée des huiles de noix de coco. R_1 et R_2 sont des groupes hydroxy-alkyle contenant entre 1 et 4 atomes de carbone.

11. Procédé selon la revendication 10, dans lequel l'agent tensioactif cationique de l'étape (a) est constitué par :

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12. Procédé selon la revendication 1, dans lequel l'agent tensioactif de l'étape (c) est $\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_4\text{H}$.

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13. Procédé selon la revendication 1, dans lequel la base organique de l'étape (c) est l'hydroxyde de tétraméthylammonium.

14. Procédé selon la revendication 1, dans lequel la base organique de l'étape (c) est l'hydroxyde de (2-hydroxyéthyl)triméthylammonium.

